

4-Methyl-N-(4-methylphenylsulfonyl)-N-phenylbenzenesulfonamide

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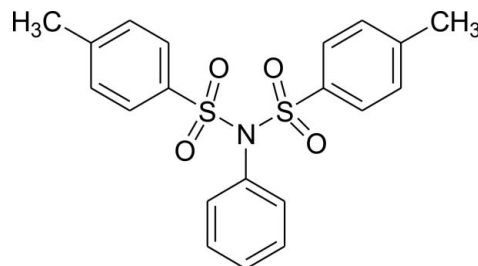
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.109; data-to-parameter ratio = 19.5.

The whole molecule of the title compound, $\text{C}_{20}\text{H}_{19}\text{NO}_4\text{S}_2$, is generated by twofold rotational symmetry. The N atom is located on the twofold rotation axis and has a trigonal-planar geometry. It is bonded by two S atoms of two symmetry-related 4-methylphenylsulfonyl groups and by the C atom of the phenyl ring, which is bisected by the twofold rotation axis. The benzene and phenyl rings are oriented at a dihedral angle of $51.48(5)^\circ$ while the pendant benzene rings are inclined to one another by $87.76(9)^\circ$. In the crystal, weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules, forming a three-dimensional network.

Related literature

Several sulfonamide derivatives have been used as chemotherapeutic agents for their antibacterial, antifungal, anti-tumor and hypoglycemic effects for many years, see: Chohan *et al.* (2010); El-Sayed *et al.* (2011); Seri *et al.* (2000). Some sulfonamide derivatives are reported to have carbonic anhydrases (CA) inhibition properties, see: Suparan *et al.* (2000). For the use of disulfonamides for their antitumor activity and CA inhibitory properties, see: Boriack-Sjodin *et al.* (1998). For the use as catalysts in asymmetric syntheses of complexes obtained from disulfonamides chiral derivatives, see: Guo *et al.* (1997). For sulfonation of aniline by 4-tolylsulfonyl chloride utilizing standard procedures with small modifications, see: DeChristopher *et al.* (1974). For a related structure involving 4-methylphenylsulfonyl, see: Elgemeie *et al.* (2013). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{20}\text{H}_{19}\text{NO}_4\text{S}_2$	$V = 1940.24(11) \text{ \AA}^3$
$M_r = 401.51$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.1080(5) \text{ \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$b = 9.3834(3) \text{ \AA}$	$T = 296 \text{ K}$
$c = 11.4821(4) \text{ \AA}$	$0.25 \times 0.22 \times 0.14 \text{ mm}$
$\beta = 96.015(3)^\circ$	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	2441 independent reflections
9411 measured reflections	1981 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	125 parameters
$wR(F^2) = 0.109$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
2441 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C6}-\text{H6}\cdots\text{O2}^i$	0.93	2.59	3.337(2)	138
$\text{C9}-\text{H9}\cdots\text{O1}^{ii}$	0.93	2.58	3.496(2)	168
$\text{C10}-\text{H10}\cdots\text{O2}^{iii}$	0.93	2.59	3.408(3)	147
$\text{C10}-\text{H10}\cdots\text{O2}^{iv}$	0.93	2.59	3.408(3)	147

Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x, -y + 1, z - \frac{1}{2}$; (iii) $x, y + 1, z$; (iv) $-x, y + 1, -z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2692).

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supporting information

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4-Methyl-*N*-(4-methylphenylsulfonyl)-*N*-phenylbenzenesulfonamide

Bilge Eren, Selçuk Demir, Hakan Dal and Tuncer Hökelek

S1. Comment

Sulfonamides, which are known as sulfa drugs, are an important class of compounds in the field of chemistry and pharmacology. Several sulfonamide derivatives are used as chemotherapeutic agents for their antibacterial, antifungal, antitumor and hypoglycemic (Chohan *et al.*, 2010; El-Sayed *et al.*, 2011; Seri *et al.*, 2000). In addition, some sulfonamide derivatives are reported to have carbonic anhydrases (CA) inhibition properties (Suparan *et al.*, 2000). Disulfonamides are sulfonamide derivatives containing two sulfone groups connected to the nitrogen atom and they are used for their antitumor activity and CA inhibitory properties (Boriack-Sjodin *et al.*, 1998). On the other hand, the complexes obtained from their chiral derivatives are used in asymmetric syntheses as catalysts (Guo *et al.*, 1997). The title compound, belonging to the disulfonimide group, was synthesized and its crystal structure is reported herein.

The asymmetric unit of the title compound contains half a molecule; the whole molecule is generated by two-fold rotational symmetry. Atoms N1, C7 and C10 are located on the two-fold rotation axis (Fig. 1). The geometry around atoms S1 and N1 are distorted tetrahedral and planar trigonal, respectively. The average S—O bond length is 1.4213 (13) Å, while the S—N and S—C bond lengths are 1.6822 (9) and 1.7546 (17), respectively. These distances are close to standard values (Allen *et al.*, 1987) and may be compared with the corresponding values in 5-amino-1-(4-methylphenylsulfonyl)-4-pyrazolin-3-one (Elgemeie *et al.*, 2013). The benzene and phenyl rings are oriented at a dihedral angle of 51.48 (5)°. Atoms S1, C11 and N1 are displaced by -0.0757 (4), -0.0172 (26) and -0.0018 (1) Å from the adjacent ring planes.

In the crystal, Fig. 2, weak C—H···O hydrogen bonds (Table 1) link the molecules into a three-dimensional network.

S2. Experimental

The title compound was prepared by a two step sulfonylation of aniline by 4-toluenesulfonyl chloride utilizing standard procedures with small modifications (DeChristopher *et al.*, 1974). Aniline (40 mmol) and benzene (10 ml) were placed in a two-necked flask fitted with a dropping funnel and a reflux condenser. A solution of 4-toluenesulfonyl chloride (20 mmol) in benzene (50 ml) was placed in the dropping funnel and was added to the aniline solution in portions with stirring. The mixture was heated under reflux for 2 h. The obtained heterogeneous mixture was cooled and the solvent was evaporated under vacuum. The crude product was treated sequentially with deionized water (20 ml) and NaOH (20%) solution. The mixture was placed in a separation funnel and the water phase was separated and acidified gently with 4M HCl. The precipitate 4-toluene sulfonanilide was collected by filtration, and then dried (yield: 3.66 g, 74%; m.p. 372–373 K). In the second step 4-toluene sulfonanilide (10 mmol) was dissolved in benzene (30 ml) and the mixture stirred under reflux. A solution of 4-toluenesulfonyl chloride (10 mmol) in benzene (30 ml) was added drop wise into the stirring solution, and then potassium tert-butoxide (12 mmol), followed by catalytic amounts of 18-crown-6 were added in portions. After the reaction system was allowed to reflux for 3 h, then the mixture was cooled and the solvent evaporated under vacuum. The crude product was treated with NaOH (20%) solution in order to remove excess 4-toluene

sulfonamide. The insoluble solids were collected by filtration, washed with deionized water, and then dried (yield: 3.21 g, 78%; m.p. 454-456 K). The suitable colourless block-like crystals were obtained by recrystallization from acetone/water (7:3).

S3. Refinement

The C-bound H-atoms were positioned geometrically with C—H = 0.93 and 0.96 Å for aromatic and methyl H-atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$, where $k = 1.5$ for methyl H-atoms and $k = 1.2$ for other H-atoms.

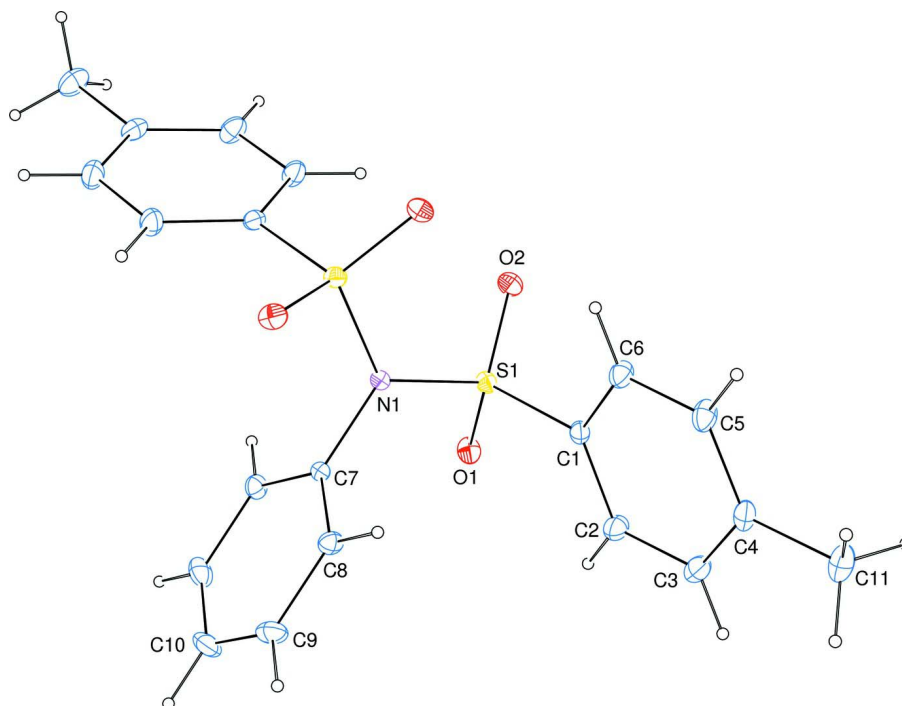


Figure 1

A view of the molecular structure of the title molecule, with atom-labelling. Displacement ellipsoids are drawn at the 50% probability level. The two-fold rotation axis bisects atoms N1, C7 and C10.

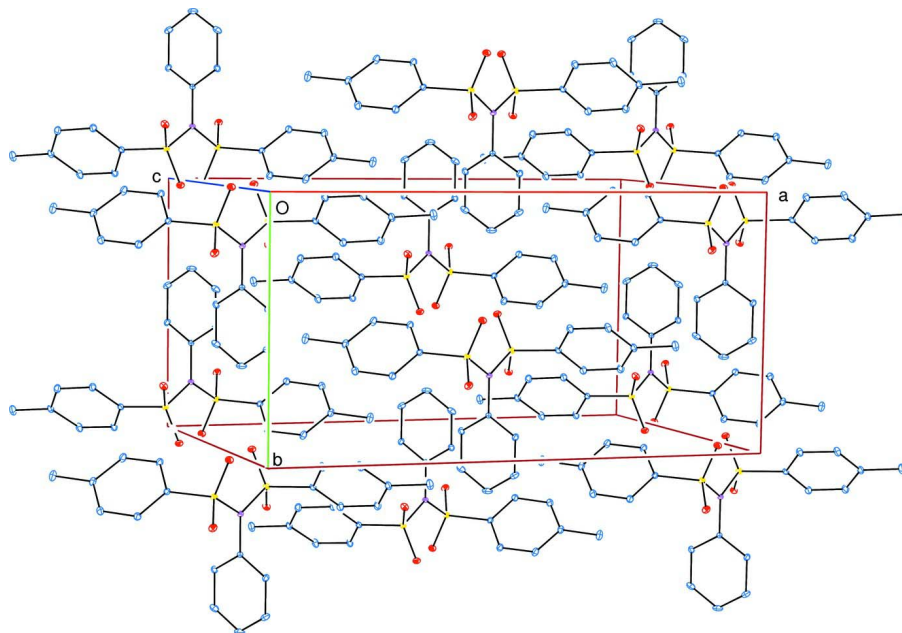


Figure 2

A partial view along the *c* axis of the crystal packing of the title compound. Hydrogen atoms have been omitted for clarity.

4-Methyl-*N*-(4-methylphenylsulfonyl)-*N*-phenylbenzenesulfonamide

Crystal data

$C_{20}H_{19}NO_4S_2$

$M_r = 401.51$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 18.1080\ (5)\ \text{\AA}$

$b = 9.3834\ (3)\ \text{\AA}$

$c = 11.4821\ (4)\ \text{\AA}$

$\beta = 96.015\ (3)^\circ$

$V = 1940.24\ (11)\ \text{\AA}^3$

$Z = 4$

$F(000) = 840$

$D_x = 1.375\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3887 reflections

$\theta = 2.3\text{--}28.1^\circ$

$\mu = 0.30\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colourless

$0.25 \times 0.22 \times 0.14\ \text{mm}$

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

9411 measured reflections

2441 independent reflections

1981 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 28.4^\circ$, $\theta_{\text{min}} = 2.3^\circ$

$h = -24 \rightarrow 23$

$k = -10 \rightarrow 12$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.109$

$S = 1.05$

2441 reflections

125 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.990P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.06888 (2)	0.13028 (4)	0.33345 (3)	0.03537 (14)
O1	0.08971 (7)	0.22464 (13)	0.42817 (10)	0.0471 (3)
O2	0.04424 (7)	-0.00962 (13)	0.35650 (11)	0.0491 (3)
N1	0.0000	0.21329 (18)	0.2500	0.0332 (4)
C1	0.14280 (9)	0.12114 (17)	0.24640 (14)	0.0369 (3)
C2	0.20477 (10)	0.2045 (2)	0.27464 (17)	0.0533 (5)
H2	0.2065	0.2682	0.3369	0.064*
C3	0.26449 (11)	0.1920 (2)	0.2089 (2)	0.0622 (5)
H3	0.3066	0.2472	0.2284	0.075*
C4	0.26270 (10)	0.0998 (2)	0.11573 (17)	0.0502 (4)
C5	0.19959 (10)	0.0185 (2)	0.08876 (17)	0.0555 (5)
H5	0.1976	-0.0443	0.0258	0.067*
C6	0.13953 (10)	0.0282 (2)	0.15261 (17)	0.0505 (4)
H6	0.0974	-0.0270	0.1330	0.061*
C7	0.0000	0.3675 (2)	0.2500	0.0303 (4)
C8	0.03282 (9)	0.43935 (18)	0.16443 (14)	0.0416 (4)
H8	0.0547	0.3897	0.1069	0.050*
C9	0.03269 (12)	0.5865 (2)	0.16553 (18)	0.0575 (5)
H9	0.0549	0.6366	0.1086	0.069*
C10	0.0000	0.6588 (3)	0.2500	0.0642 (8)
H10	0.0000	0.7579	0.2500	0.077*
C11	0.32811 (12)	0.0864 (3)	0.0452 (2)	0.0711 (6)
H11A	0.3110	0.0578	-0.0333	0.107*
H11B	0.3620	0.0163	0.0805	0.107*
H11C	0.3529	0.1767	0.0435	0.107*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0368 (2)	0.0329 (2)	0.0360 (2)	0.00350 (15)	0.00149 (15)	0.00050 (14)
O1	0.0507 (7)	0.0514 (7)	0.0377 (6)	0.0076 (6)	-0.0026 (5)	-0.0083 (5)

O2	0.0542 (7)	0.0365 (7)	0.0565 (7)	0.0010 (5)	0.0051 (6)	0.0118 (5)
N1	0.0307 (9)	0.0270 (9)	0.0416 (9)	0.000	0.0019 (7)	0.000
C1	0.0326 (7)	0.0355 (8)	0.0421 (8)	0.0054 (6)	0.0014 (6)	-0.0017 (6)
C2	0.0428 (10)	0.0543 (12)	0.0634 (11)	-0.0051 (8)	0.0085 (8)	-0.0180 (9)
C3	0.0400 (10)	0.0637 (14)	0.0836 (14)	-0.0079 (9)	0.0102 (9)	-0.0130 (11)
C4	0.0383 (9)	0.0586 (11)	0.0542 (10)	0.0136 (8)	0.0077 (8)	0.0061 (9)
C5	0.0433 (10)	0.0721 (13)	0.0507 (10)	0.0088 (9)	0.0036 (8)	-0.0189 (9)
C6	0.0373 (9)	0.0587 (11)	0.0551 (10)	0.0005 (8)	0.0023 (7)	-0.0181 (9)
C7	0.0289 (9)	0.0271 (10)	0.0353 (10)	0.000	0.0052 (8)	0.000
C8	0.0416 (9)	0.0435 (10)	0.0412 (8)	-0.0051 (7)	0.0116 (7)	0.0032 (7)
C9	0.0655 (13)	0.0455 (11)	0.0606 (11)	-0.0167 (10)	0.0013 (9)	0.0166 (9)
C10	0.076 (2)	0.0270 (13)	0.084 (2)	0.000	-0.0178 (17)	0.000
C11	0.0481 (11)	0.0943 (18)	0.0736 (14)	0.0158 (12)	0.0198 (10)	0.0051 (13)

Geometric parameters (Å, °)

S1—O1	1.4223 (12)	C6—C5	1.377 (3)
S1—O2	1.4203 (13)	C6—H6	0.9300
S1—N1	1.6822 (9)	C7—N1	1.447 (3)
S1—C1	1.7546 (17)	C7—C8 ⁱ	1.3768 (18)
N1—S1 ⁱ	1.6822 (9)	C7—C8	1.3768 (18)
C1—C2	1.378 (2)	C8—C9	1.380 (3)
C1—C6	1.382 (2)	C8—H8	0.9300
C2—C3	1.387 (3)	C9—C10	1.368 (3)
C2—H2	0.9300	C9—H9	0.9300
C3—H3	0.9300	C10—C9 ⁱ	1.368 (3)
C4—C3	1.374 (3)	C10—H10	0.9300
C4—C5	1.382 (3)	C11—H11A	0.9600
C4—C11	1.508 (3)	C11—H11B	0.9600
C5—H5	0.9300	C11—H11C	0.9600
O1—S1—N1	105.59 (7)	C6—C5—H5	119.2
O1—S1—C1	108.00 (8)	C1—C6—H6	120.5
O2—S1—O1	119.74 (8)	C5—C6—C1	118.97 (17)
O2—S1—N1	107.79 (8)	C5—C6—H6	120.5
O2—S1—C1	109.53 (8)	C8 ⁱ —C7—N1	119.33 (10)
N1—S1—C1	105.22 (5)	C8—C7—N1	119.33 (10)
S1 ⁱ —N1—S1	124.83 (11)	C8 ⁱ —C7—C8	121.3 (2)
C7—N1—S1	117.58 (5)	C7—C8—C9	118.82 (17)
C7—N1—S1 ⁱ	117.58 (5)	C7—C8—H8	120.6
C2—C1—S1	119.29 (13)	C9—C8—H8	120.6
C2—C1—C6	120.59 (16)	C8—C9—H9	119.9
C6—C1—S1	120.10 (13)	C10—C9—C8	120.26 (19)
C1—C2—C3	119.09 (17)	C10—C9—H9	119.9
C1—C2—H2	120.5	C9 ⁱ —C10—C9	120.5 (3)
C3—C2—H2	120.5	C9 ⁱ —C10—H10	119.8
C2—C3—H3	119.3	C9—C10—H10	119.8
C4—C3—C2	121.38 (18)	C4—C11—H11A	109.5

C4—C3—H3	119.3	C4—C11—H11B	109.5
C3—C4—C5	118.27 (17)	C4—C11—H11C	109.5
C3—C4—C11	120.97 (19)	H11A—C11—H11B	109.5
C5—C4—C11	120.76 (19)	H11A—C11—H11C	109.5
C4—C5—H5	119.2	H11B—C11—H11C	109.5
C6—C5—C4	121.70 (17)		
O1—S1—N1—S1 ⁱ	-151.02 (6)	C2—C1—C6—C5	0.9 (3)
O1—S1—N1—C7	28.98 (6)	C1—C2—C3—C4	0.8 (3)
O2—S1—N1—S1 ⁱ	-21.94 (6)	C5—C4—C3—C2	-0.2 (3)
O2—S1—N1—C7	158.06 (6)	C11—C4—C3—C2	-179.7 (2)
C1—S1—N1—S1 ⁱ	94.88 (6)	C3—C4—C5—C6	-0.1 (3)
C1—S1—N1—C7	-85.12 (6)	C11—C4—C5—C6	179.42 (19)
O1—S1—C1—C2	-3.00 (17)	C1—C6—C5—C4	-0.3 (3)
O1—S1—C1—C6	175.15 (14)	C8—C7—N1—S1	94.21 (8)
O2—S1—C1—C2	-134.97 (15)	C8 ⁱ —C7—N1—S1	-85.79 (8)
O2—S1—C1—C6	43.18 (16)	C8—C7—N1—S1 ⁱ	-85.79 (8)
N1—S1—C1—C2	109.41 (15)	C8 ⁱ —C7—N1—S1 ⁱ	94.21 (8)
N1—S1—C1—C6	-72.44 (16)	N1—C7—C8—C9	-179.79 (12)
S1—C1—C2—C3	177.00 (16)	C8 ⁱ —C7—C8—C9	0.21 (12)
C6—C1—C2—C3	-1.1 (3)	C7—C8—C9—C10	-0.4 (2)
S1—C1—C6—C5	-177.22 (15)	C8—C9—C10—C9 ⁱ	0.21 (13)

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots O2 ⁱ	0.93	2.59	3.337 (2)	138
C9—H9 \cdots O1 ⁱⁱ	0.93	2.58	3.496 (2)	168
C10—H10 \cdots O2 ⁱⁱⁱ	0.93	2.59	3.408 (3)	147
C10—H10 \cdots O2 ^{iv}	0.93	2.59	3.408 (3)	147

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $x, -y+1, z-1/2$; (iii) $x, y+1, z$; (iv) $-x, y+1, -z+1/2$.